

## [III-25]

### Surface Structural Study of the disordered chlorinated Ti(0001) Surface by Diffuse Low Energy Electron Diffraction

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#### I. Introduction

The determination of surface crystallography by low-energy electron diffraction (LEED) has traditionally been limited to surfaces that are well ordered. However, it has recently become possible to investigate the structure of disordered adsorbates thanks to the development of a theory of diffuse low-energy electron diffraction (DLEED), but as yet only a small number of systems have been studied using this technique. Previous work in this laboratory has shown that exposure of a Ti(0001) surface to chlorine gas at room-temperature results in a LEED pattern that is unchanged from that of the clean surface, except for an increase in the background diffuse scattered intensity. Annealing a saturation dose at elevated temperatures does result in a new LEED pattern that we have ascribed as being due to a coincidence structure. However, low coverages of chlorine do not order upon annealing, but remain disordered. We have therefore applied the DLEED method to disordered chlorine adsorbed on the Ti(0001) surface and succeeded in identifying the adsorption site and bond length.

#### II. Experimental

The experiments were carried out in an ion-pumped UHV system with a base pressure  $< 3 \times 10^{-10}$  torr, containing four-grid LEED/Auger optics and a quadrupole mass spectrometer. The Ti crystal was cleaned by repeated cycles of ion bombardment at 600°C and annealing at 750°C. This treatment was necessary to remove bulk sulfur impurities and keep the crystal from the phase transition while not depositing carbon from the background.

Chlorine was then deposited at, or below, room temperature from the solid state electrochemical source. The LEED patterns observed after the passage of up to 250  $\mu\text{C}$  of charge passed through the cell (about 0.4 ML chlorine coverage) did not show any change from the hexagonal pattern of the clean Ti(0001) surface, other than an increase in the diffuse background. DLEED data were taken as quickly as possible after dosing using a sensitive silicon-intensified video camera, interfaced to an image grabber/processing card. The screen images were rapidly transferred to video tape for later analysis, resulting in a total data collection time of less than 10 min.

#### III. Results and Discussion

The diffuse LEED data were extracted from the raw data to remove the elastic scattering and diffuse scattering due to crystal defects and thermal scattering from the substrate by subtracting the diffuse intensity pattern of the clean surface taken at the same temperature. The Pendry Y-function of the data was then constructed by using two sets of experimental data taken at closely spaced energies (4 eV apart).

The experimental Y-functions were then compared with theoretical Y-functions calculated from various types of adsorption site and bond length, using the Pendry R-factor. The calculations also allowed the Ti-Cl interlayer distance to vary, but fixed other structural parameters. Using the Pendry R-factor, the on-top and bridge sites are easily rejected, but the two types of 3-fold sites cannot be distinguished.

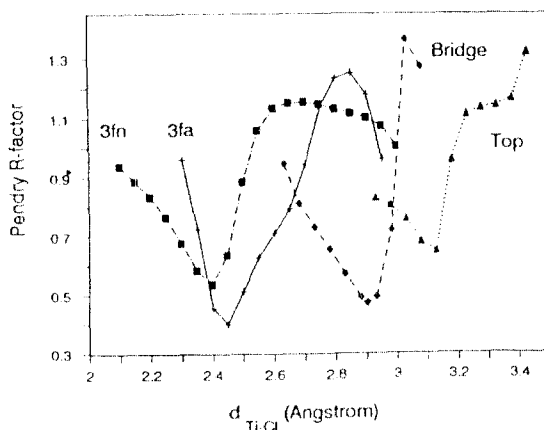


Fig. 1 Analysis of the (78,82)-eV energy pair DLEED data for 0.2 ML Cl/Ti(0001) at 173 K using the Pendry R-factor, for the four adsorption sites.

Table 1 Results of an R-factor analysis for Cl/Ti(0001) at 0.2 ML coverage.

Site	$R_p$ (min)	$d_{Ti-Cl}$ (min) (Å)	Ti-Cl bond length (Å)
A-1F	0.649	3.13	3.13
B-2F	0.471	2.90	3.25
C-3Fa	0.405	2.45	2.98
D-3Fn	0.536	2.40	2.94

#### IV. Conclusion

Molecular chlorine adsorbs dissociatively on the clean Ti(0001) surface to form a disordered overlayer that only orders after high temperature annealing. DLEED intensities were measured using a low-light level video camera system from 0.2ML of atomic chlorine adsorbed at 173K on Ti(0001). An analysis of the Pendry Y-functions for (78, 92) and (90, 94)- eV energy pairs employing Pendry R-factor shows that the chlorine atom is adsorbed in a three fold hollow site on the Ti surface with a Ti-Cl interlayer spacing of  $2.48 \pm 0.07$  Å. These results indicate a Ti-Cl bond length of 2.96 Å which is good agreement with the value of 2.94 Å predicted from solid state chemistry considerations.